REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
14-10-2008

2. REPORT TYPE
Technical Paper

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Ignition Characteristics of Single-Walled Carbon Nanotubes (SWCNTs) Utilizing a Camera Flash for Distributed Ignition of Liquid Sprays (Preprint)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
B. Chehroudi (ERC); S.A. Danczyk (AFRL/RZSA); C. Morgan (AFRL/RZSE);
Alan Badakhshan (Jacobs)

5d. PROJECT NUMBER

5e. TASK NUMBER
43470876

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RZSA
10 E. Saturn Blvd.
Edwards AFB CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-RZ-ED-TP-2008-423

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RZS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-RZ-ED-TP-2008-423

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA #08399A).

13. SUPPLEMENTARY NOTES
For presentation at the 55th JANNAF Propulsion/4th LPS/3rd SPS/6th MSS Joint Meeting, to be held in Orlando, FL, 8-12 Dec 2008.

14. ABSTRACT

We have studied ignition characteristics of SWCNTs with an ordinary camera flash. Our ultimate goal is to use SWCNTs as a means for ignition of liquid rocket fuel sprays. Based on the initial results, we believe this approach enables volumetric and distributed ignition of fuel sprays. Our preliminary investigation was concentrated on the effects of two different incident light source pulse widths on minimum ignition energy (MIE) from 350-1500 nm, effects of degree of sample compactness (packing) on the ignition characteristics, effects of percent iron (Fe) content of the SWCNTs samples, and initial measurements of sound pressure level (SPL) from the photo acoustic phenomenon. Our results indicate that the shorter pulse width (with lower energy/pulse) required ~30-35 mJ/pulse to initiate ignition of the un-compacted samples in standard air whereas the longer pulse width (with higher energy/pulse) needed ~80-90 mJ/pulse to achieve the same results. For lightly-compressed samples, MIE remains unchanged; otherwise it increases with increased level of compression. Our results suggest that samples with less than 30% Fe content (by weight) cannot be ignited with the utilized camera flash in air. Additionally, we found interesting photo-acoustic behavior and some other novel phenomena associated with radiation absorption by SWCNTs.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Dr. Stephen A. Danczyk
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*
Unclassified	**Unclassified**	**Unclassified**	SAR	8	N/A

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

Ignition Characteristics of Single-Walled Carbon Nanotubes (SWCNTs) Utilizing a Camera Flash for Distributed Ignition of Liquid Sprays (Preprint)

B. Chehroudi[1], S.A. Danczyk[2], C. Morgan[3], and A. Badakhshan[4]

Air Force Research Laboratory/ PRSA
10E Saturn Blvd
Edwards AFB, CA 93524-7680

Abstract

We have studied ignition characteristics of SWCNTs with an ordinary camera flash. Our ultimate goal is to use SWCNTs as a means for ignition of liquid rocket fuel sprays. Based on the initial results, we believe this approach enables volumetric and distributed ignition of fuel sprays. Our preliminary investigation was concentrated on the effects of two different incident light source pulse widths on minimum ignition energy (MIE) from 350-1500 nm, effects of degree of sample compactness (packing) on the ignition characteristics, effects of percent iron (Fe) content of the SWCNTs samples, and initial measurements of sound pressure level (SPL) from the photo acoustic phenomenon. Our results indicate that the shorter pulse width (with lower energy/pulse) required ~30-35 mJ/pulse to initiate ignition of the un-compacted samples in standard air whereas the longer pulse width (with higher energy/pulse) needed ~80-90 mJ/pulse to achieve the same results. For lightly-compressed samples, MIE remains unchanged; otherwise it increases with increased level of compression. Our results suggest that samples with less than 30% Fe content (by weight) can not be ignited with the utilized camera flash in air. Additionally, we found interesting photo-acoustic behavior and some other novel phenomena associated with radiation absorption by SWCNTs.

Introduction

The ignition of SWCNTs caused by an ordinary camera flash at close ranges was first observed In 2002 by Ajayan, et al. [1] The work by Smits et al. [2] suggested that Fe nanoparticles within the as-produced SWCNTs are playing an important role in the ignition process. Subsequently, Chehroudi and Danczyk [3, 4, 5, 6] reproduced some of the aforementioned results and in addition demonstrated that SWCNTs could be used as ignition agents for a variety of liquid fuels, including those of interest in liquid rocket engines. They also suggested that SWCNTs could facilitate distributed ignition of liquid sprays. Below, we will describe the experimental setup and procedure followed by the preliminary results.

Experimental Setup and Instrumentation

The basic experimental setup consists of a Vivitar camera flash, model number 730AFN, as ignition light source, a pulse energy meter from GenTec, SUN series EM-1 with ED-500 detector head, a sensitive microphone from Piezotronic Inc. model S05692 for detection of photo-acoustic signal, an XYZ traversing stage with a filter wheel for introducing optical filters within the light path. The light source (i.e., camera flash), a pulsed Xe arc lamp with 0.1 and 9 ms durations at low and high light energy settings, was coupled to the sample area through a 3'x½" quartz fiber optic light guide from Sunoptics Technologies. A high-resolution Canon digital camera was used to capture the images of samples before and after they were exposed to a flash of light for ignition process characterization purposes. The Z-traverse (i.e., vertical) direction of the XYZ stage provided a means for incremental change in the energy-per-pulse experienced by the sample. Samples of the SWCNTs were purchased from Unidym Corp, Houston, Texas.

A complete experimental setup, part of which to be used in our future investigations, is shown in Fig. 1. It includes additional instrumentation in order to expand our measurement capabilities. A high-speed pyrometer from Mikron model number KGA 740 HS, covering from 300-2300º C is used to determine the temperature of the sample as a function of time. The fiber coupled NIR spectrometer, model Symphony HR320 from Horiba, covering from 600-1400 nm is used to measure the spectral emission of the sample with and without ignition. A high-speed camera model Phantom V7.1 from Vision System which is capable of capturing up to 4000 frames/s, full screen, is used to take a snapshot of ignition process.

The data acquisition system, Win600 16 channel digital scope/DAQ system from Hi-Techniques, is supplemented with a photodiode detector to detect the light from the camera flash and provide a TTL event synchronization pulse through a digital delay/pulse generator. The DAQ system allows the synchronization between all of the detection systems in addition to registration of the signal for the photometer, the pyrometer and the microphone. The entire experimental setup is housed inside a fume hood and the ventilation is turned on as needed.

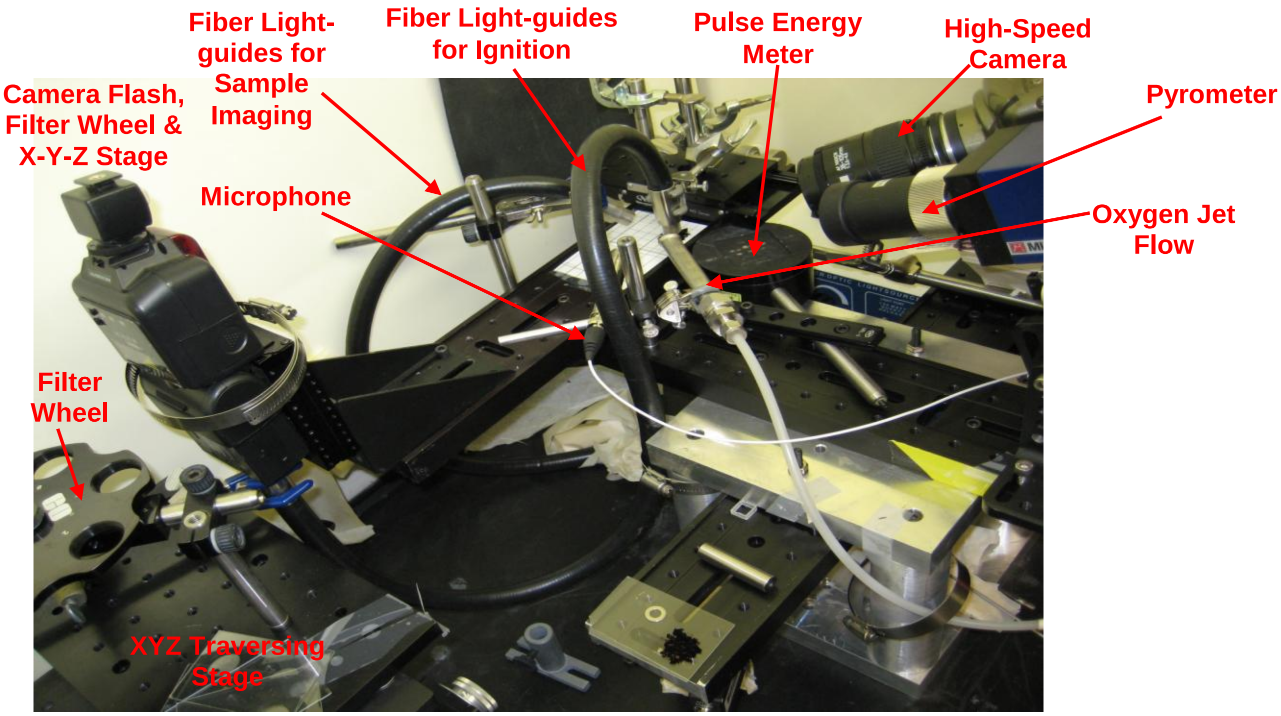

Figure 1– The experimental set up for the study of photo-ignition effect in SWCNT. Digital camera and the fiber coupling for the spectrometer are not shown. A sample on a 2"x3" glass slide is also shown in the lower part of this picture

Experimental Procedure

Safety was paramount in our tests and for this reason all the necessary personal protection equipments (PPEs) such as proper gloves, respirators, head and face special tissue cover, laboratory coats, and goggles were worn. Samples of SWCNTs are very carefully removed from their original containers and slowly laid on a microscope objective positioned near the end of the fiber optic cable. Then the slide was slowly pushed towards the test area where the end of the fiber optic cable is positioned. There is a grid-lined paper in that area (seen later in images of samples) where identifies the precise location of the sample and also used for length scale calibration purposed.

The output end fiber optic light guide is attached to a traversing stage so that if can be easily moved over sensing area of the light energy meter for measurement of energy/pulse. The distance between the sensing element and the end of the fiber optic is kept the same as that distance between the fiber end and the SWCNTs sample. This way, the energy per pulse measured by the sensor is the same as that applied to the sample. The ignition test started with an energy/pulse well below the energy required for ignition and it is progressively increased at discrete steps until the onset of ignition and beyond. At each step, energy per pulse was measured and images of the sample were taken before and after the application of each flash pulse. This way, we have a detailed characterization of the ignition process. The onset of ignition is usually sharply and easily identifiable with un-compacted and lightly compacted samples.

Experimental Results and Discussion:

We studied ignition characteristics of SWCNTs as a function of flash pulse duration, wavelength of light, compaction force, Fe content, and the correlation between the photo-acoustic effect and ignition process. The study of ignition characteristics of compacted sample was performed in air and in an oxygen-rich environment. It is worth mentioning that we also performed a preliminary study of the ignition process through simultaneous time-resolved measurement of temperature (pyrometer), NIR spectra, high-speed movie, and photoacoustic effect. However, results will be published in another future paper.

Effects of Flash Pulse Width and Light Wavelength on SWCNTs' Ignition Process

As-produced samples of SWCNTs with 50% Fe contents were used for this study. These samples are "fluffy" in appearance and easily fluidized in air. For this reason, individuals handling these samples should take extra precautions to prevent inadvertent spread and human exposure. In tests conducted here, the energy per pulse is increased progressively from a very low

value and according to the procedure explained above until a sudden (and distributed) ignition at multiple locations is observed in the sample. The flash pulse energy on the sample at this point is the minimum ignition energy needed for the ignition of the as-produced SWCNTs samples. Table 1 shows a summary of our preliminary results. We observed that regardless of optical filter in use i.e., the selected incident wavelength region, the minimum energy/pulse needed for the onset of ignition only depends on the pulse width of the flash. This can be seen by comparing pairs of results with the same filters in Table 1. For the low energy/light setting (corresponds to a shorter pulse width of 0.1 ms) the minimum ignition energy is 30-35 mJ/pulse and about 80-95 mJ/pulse for the energy/high setting (corresponds to a much longer pulse width of 9 ms).

Table 1 also meant to indicate results from a number of optical filters to investigate impact of the wavelength. However, because of limited data, it is our plan to investigate the impact of different wavelength regions in a more refined and systematic manner and the results will be presented in another publication. Nevertheless, preliminary data shown in table 1 suggests that there is no sizable effect of the wavelength of light instead the speed with which a certain amount of light energy is delivered to the sample plays an important role. Specifically, it is shown that a lower amount of energy (~30-35 mJ) is able to initiate ignition if the sample is exposed at a shorter duration. This is intuitively reasonable because at shorter pulse duration (low flash setting), the energy transfer time constant is comparatively shorter than the time constant for energy (heat) losses from the sample (primarily through conduction, assuming same spectral coverage).

Table 1- Measured Minimum Ignition Energy (MIE) per pulse and calculated power per unit area on the sample for different filters. The same exposure footprints are assumed for both low and high energy settings. LP and SP stand for long pass and short pass filters.

	FILTERS USED	**Photo-Ignition /Photo-Acoustic**	**MIE (mJ/pulse)/ (W/cm2)**	**Flash Energy Setting/ Pulse Duration (ms)**	**Max Light Output @ This Filter & Flash Setting (mJ/pulse)**
1	No filter used	Yes/yes	81±15 / 7.3 ±1.4	High /9	620
2	Same as above	Yes/yes	32±5 / 255 ±40	Low /0.1	54
3	LP 495-nm, CVI	Yes/yes	83±15 / 7.5	High /9	460
4	Same as above	Yes/yes	36±5 / 290	Low /0.1	44
5	LP 550-nm, CVI	Yes/yes	97±15 / 8.7	High /9	425
6	Same as above	Yes/yes	33±5 / 260	Low /0.1	34
7	SP 1100-nm, Edm.	Yes/yes	79±15 / 7.1	High /9	505
8	Same as above	Yes/yes	29±5 / 230	Low /0.1	45
9	LP 700-nm, Edm.	Yes/yes	83±15 / 7.5	High /9	440
10	Same as above	Yes/yes	32±5 / 255	Low /0.1	39
11	SP 900-nm, Edm.	Yes/yes	85±15 / 7.7	High /9	385
12	Same as above	Yes/yes	32±5 / 255	Low /0.1	34
13	Many other filters	Yes/yes	80±15 / 7-8	High /9	N/A
14	Same as above	No/No	Not Applicable	Low /0.1	below 30

The Ignition Characteristics of Compacted SWCNT Samples

In some real-life applications of SWCNTs as ignition agents, one may need to produce small pellets or films of SWCNTs by a compaction process. One wonders as to what extent the compaction process may affect the ignition characteristics of the as-produced SWCNTs. To investigate this, samples are sandwiched in between two 2"x3" microscope glass slides and a known amount of weight was applied to the sample sandwich in a uniformly distributed manner. Then the slides were separated and ignition tests were performed in air and in an oxygen-rich environment using the same procedure described for samples with no compaction (i.e., un-compacted and fluffy samples). We studied samples with a wide range of compaction and determined the ignition characteristics for each.

The ignition process is monitored and characterized by measurements of the percent (or fraction) of the exposed sample area covered with "orange dots or clusters", being indicative of iron oxide particles due to interaction of the light and the SWCNTs sample. High-resolution images taken before and after application of each flash pulse at a given energy/pulse level combined with image processing methods enabled quantification of the observed feature. One distinct difference, with the exception of lightly-loaded samples, is that no abrupt or sudden ignition of the SWCNTs samples is observed (as seen for the un- compacted fluffy samples) and the impact of the ignition process is progressive and gradual in nature. Figure 3 shows the gradual ignition process in a compacted sample (10 lb applied force) in air. These pictures are taken after exposure of 25 (left image) and 30 (right image) progressively more energetic pulses of light (as the Z dimension of the XYZ traversing stage is varied) on the same sample. Note that the ignition process, characterized by the concentration of orange dots or clusters, slowly develops with each exposure, and the ignited region of the sample is limited to the circular footprint of the light-exposed area.

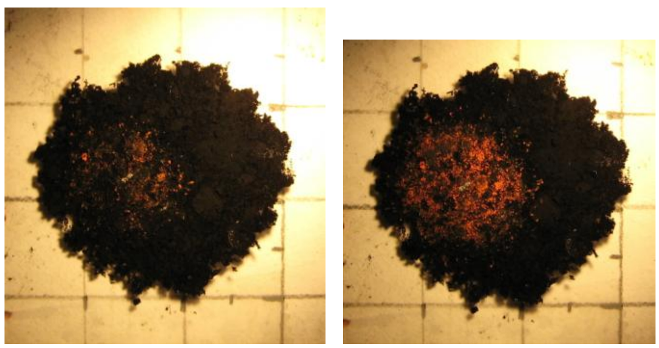

Figure 3- Example of ignition process in a compressed sample (10 lb weight on the slide sandwich) in the air. The picture on the left is due to 25 successively-increasing flash energy exposures and the right one shows the same sample after 30 exposures. The orange area represents the region that has been illuminated by light output from the end of the fiber optic cable.

Figure 4 shows plots of the fraction of the illuminated sample area that is covered with orange dots (i.e., iron oxides) as a function of the energy per pulse for high setting of the camera flash with wider pulse width of ~ 9ms. We have used the high setting because we expected the need for progressively higher energy/pulse as the level of compaction increased. We were unable to carry on the same set of experiments at low flash setting (shorter pulse duration), because of the much lower maximum possible output energy/pulse at this setting. Hence our investigation was limited to the high energy setting (long pulse duration) for this initial results. Nevertheless, we found that the lightly-compacted samples (with weights of ~0.35 lb) exhibited the same ignition characteristics as the un-compacted fluffy samples.

As expected, we found that samples with a higher degree of compaction required considerably higher energy per pulse to achieve the same concentration of the orange-colored iron oxide particles obtained by visual inspection. The ignition of compacted samples, as opposed to un-compacted (fluffy) and lightly-compacted (with a compaction force of 0.35 lb) samples, is very gradual and less well-defined. The concept of minimum ignition energy, though valid given the abrupt nature of ignition of the un-compacted (fluffy) samples, is not quite appropriate here. For this reason, we took images before and after each flash pulse exposure and performed extensive image analysis in order to determine the iron oxide area fraction as it is assumed correlated with faction of the sample that has been ignited. The build up of iron oxide, an indication of the ignition process, is more gradual for the 5-15 lb compaction range and it is much more gradual for the 20-30 lb compaction force range. For example, for the latter case, no detectable iron oxide regions are seen even up to when a 400 mJ/pulse is applied.

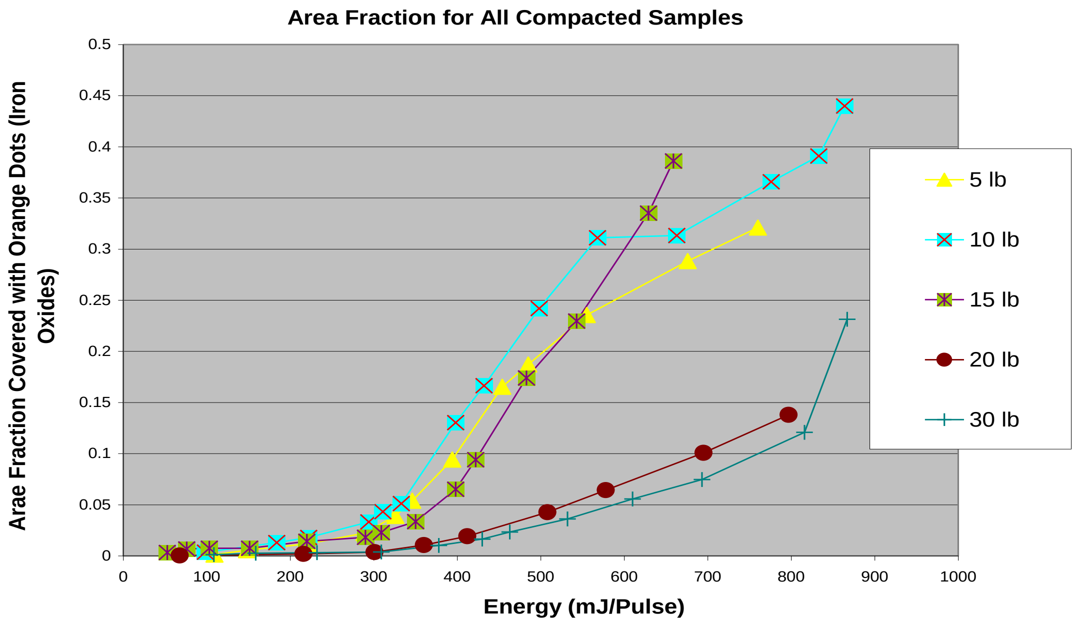

Figure 4- Ignition characteristics of moderately and heavily compacted samples at high setting of the camera flash with wider pulse duration of ~9ms. These plots show the area fraction of the illuminated area that is covered with iron oxide (orange dots).

The Effect of Oxygen-Rich environment on Ignition Process of Compacted Samples

In a real world applications of SWCNTs as ignition agents, we expect operation in an O_2-enriched environment within certain regions of the combustion chamber. Hence, we studied the effect of O_2 flow on ignition characteristics of compacted SWCNT samples. The steady flow of oxygen arranged for this study, though very low, is however high enough to blow the fluffy un-compacted sample away from the test area. This made tests with fluffy powders of SWCNTs almost impossible. Hence, lightly-compacted samples with a compaction force of 0.35 lb were used as representative of uncompacted (fluffy) samples because through many tests we were convinced that their ignition characteristics were the same.

Figure 5 shows a typical example of the ignition process with oxygen flowing over the samples. The ignition occurs suddenly, it covers most of the exposed surface area, and the iron oxide regions look full, solid, and fused together compared to scattered orange particulates/clusters seen in Fig. 3. Note that the precise concentration of the oxygen generated by the oxygen flow as compared to standard atmosphere is not known at this stage and the purpose of the test was simply to qualitatively assess gross changes in ignition behavior.

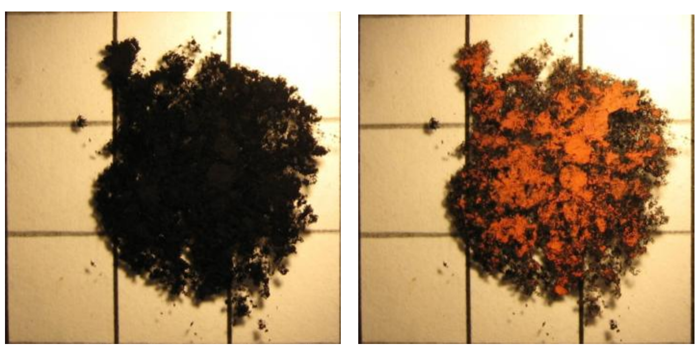

Figure 5- Shows the observed rapid and abrupt ignition process for a compressed sample (10 lb) in an oxygen-rich environment at the 8th (before ignition event on the left) and 9th (after ignition onset on the right) pulse when a series of pulses with increasingly more energy/pulse is used. The camera flash setting was at high.

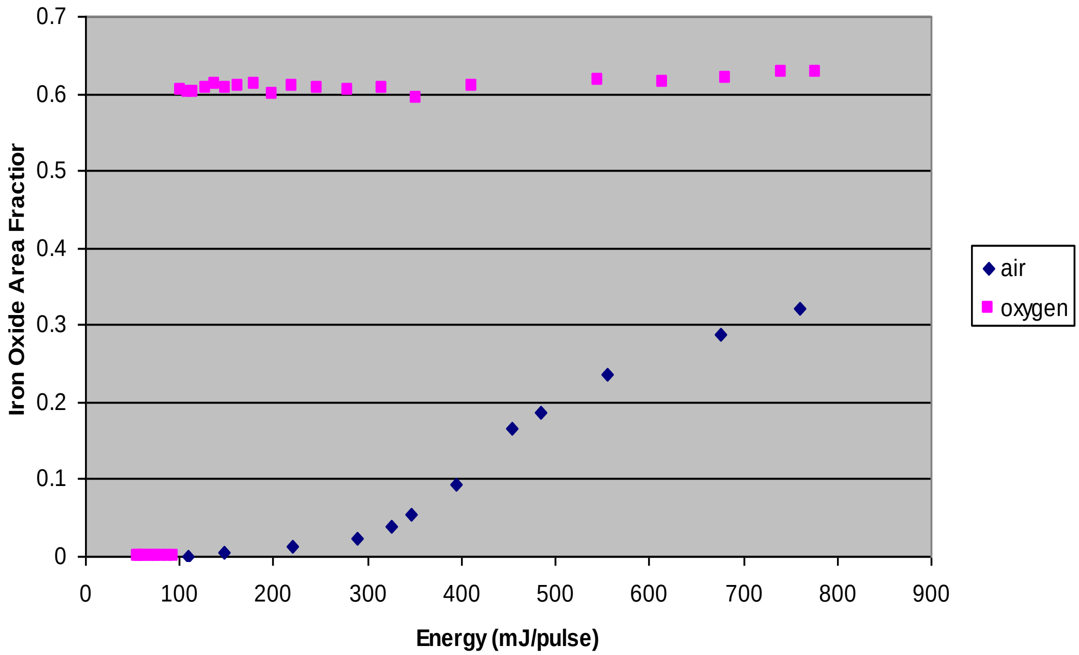

Figure 6- Ignition characteristics of a compacted sample (5 lb) under air and oxygen-rich environments at the high flash setting. Plot shows illuminated area fraction that is covered with orange dots (i.e., iron oxides).

Our findings show that oxygen-enriched environment markedly improves the ignition process so that a large part of the sample ignites with a single flash above certain well-defined minimum ignition energy (per pulse). Typically, more than 50% of the surface of the sample is covered with iron oxide after the onset of ignition and it extends beyond the circular light exposure footprint which is defined by the diameter of the fiber light-guide. We also found that samples with a wide range of compaction loads fully ignite within the same energy range of110 ± 20 mJ/pulse. Figure 6 shows an example of the ignition characteristic in air and in oxygen-rich environments. The abrupt nature of the ignition process under excess oxygen is clearly seen by a jump in iron oxide area fraction at about 110 mJ/pulse point.

The Effect of Fe Concentration on SWCNTs Ignition

We studies minimum ignition energy for four samples with different Fe concentrations. In addition to Fe content, these samples look very different as well. The samples with higher Fe content are fluffy and look velvet black, while the samples with lower Fe content are granular and they look dark gray/black. The results of this study are summarized in the following table.

Table 2- Minimum Ignition energy for SWCNT samples with different Fe content in air. The high energy setting of the camera flash, which also corresponds with a much longer flash duration was used for all of the experiments.

Sample Code	**Fe Content of Sample (%)**	**Sample Appearance**	**Igni. Energy Trial 1 (mJ/pulse)**	**Igni. Energy Trial 2, (mJ/pulse)**
R0215	50	like soot, velvet black	85* ± 10	85* ± 10
R0220	30	like soot, velvet black	152 ± 15	148 ± 15
P0232	12	gray/black powder	>1140	>2500**
D0381	8	gray/black powder	>1100	>2500**

*These are the average of many trials
“> 1100” means no ignition was observed up to the value shown
**used a different camera flash with 2x4 cm2 area and total output of 6 J/pulse

Correlation Between Photo-acoustic Effect and Ignition Threshold

We began a systematic study of the photoacoustic effect for many SWCNTs samples. The popping sound, heard at the time of the application of each flash of light, more or less exists with or without ignition. This was recorded by a microphone and the sound pressure level (SPL) calculated. For each sample, the SPL was produced as a function of photon energy level, to be referred as photoacoustic curve. The photoacoustic behavior and photo ignition process were characterized through application of a series of flashes with successively increasing energy per pulses.

Figure 7 shows the correlation between photo acoustic effect and photo-ignition for a sample that was compacted with a force of 15 lb. The two sets of data appear to indicate the same trend in their change of slope and this happens around the region of energy where the ignition process accelerates. This is evidenced by the steepened slope of the line representing the iron oxide area fraction as a function of the light source energy per pulse.

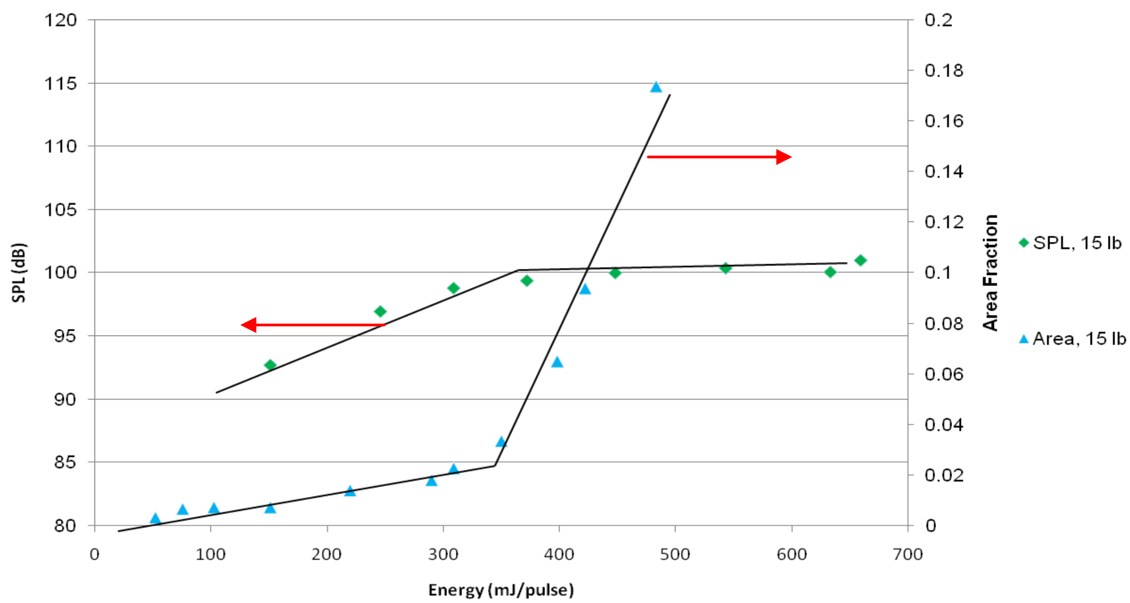

Figure 7- Correlation between photo acoustic effect (measured as SPL) and photo-ignition for a sample with a compaction force of 15 lb with high energy flash which also has longer pulse duration. The arrows show the corresponding axes for each curve.

Conclusions

SWCNTs can be easily ignited in distributed manner with a low-level Xenon pulsed source such as a camera flash. We studied minimum ignition energy for the un-compacted fluffy (or very lightly compacted) samples as a function of flash pulse duration. We found that the pulse width played an important role in determining the minimum ignition energy. As expected, samples with a higher degree of compaction require considerably higher energy per pulse for ignition. Moreover, the ignition process is very gradual and less well-defined in moderately- and heavily- compacted samples. We found that this problem is dramatically reduced in an oxygen-rich environment. Initial investigation of the effects of the wavelength showed no noticeable change in minimum ignition energy for any wavelength region. However, further studies are justified and will be conducted. The photo-acoustic effect measured via a microphone correlates well with the observed photo ignition characteristics.

References

1. Ajayan, P.M., et al., *Science* 296, 705, 2002.
2. Smits, J., et al., *Material Science and Engineering* A358, 384 –389, 2003.
3. Chehroudi, B., et al., A Method for distributed ignition of fuels by low-energy light sources, USPTO, Patent Pending, 2004.
4. Danczyk, S. A. and Chehroudi, B., Nano Science and Technology Institute Conference, Anaheim, California, May 8-12, 2005.
5. Danczyk, S. A. and Chehroudi, B., *53ed JANNAF Meeting*, Monterey, California, Dec. 5-8, 2005.
6. *Coverage of nanotube ignition* work by the *New Scientist Magazine* entitled, "Forget Spark Plugs, Start Your Engine with Nanotube", Nov 19, 2005 issue.